

Macro- and micronutrient-release characteristics of three polymer-coated fertilizers: Theory and measurements

Curtis Adams^{1*}, Jonathan Frantz², and Bruce Bugbee¹

¹ Department of Plants, Soils, and Climate, Utah State University, 4820 Old Main Hill, Logan, UT 84322, USA

² Greenhouse Production Research Group, USDA-ARS, 2801 W. Bancroft St., Mail Stop 604, Toledo, OH 43606, USA

Abstract

In spite of several published studies we have an incomplete understanding of the ion-release mechanisms and characteristics of polymer-coated fertilizers (PCF). Here we extend current conceptual models describing release mechanisms and describe the critical effects of substrate moisture and temperature on macro- and micronutrient release of three PCF types: Polyon[®], Nutricote[®], and Osmocote[®]. Nutrient release was quantified at weekly intervals for up to 300 d from 5°C to 40°C in water and chemically inert sand, substrates that allowed release quantification without confounding effects of ion sorption/desorption. At least two release-timeframe formulations of each PCF type were studied and all products had similar nutrient concentrations to allow isolation of the effect of coating technology. Contrary to several studies, our data and model indicate that there is no significant difference in nutrient-release rates in water and a moist, solid substrate. This means that release rates determined in water can be used to model bio-available nutrient concentrations in moist soil or soilless media where sorption/desorption properties alter concentrations after release. Across all PCF, the nutrients most affected by temperature were typically N, K, B, Cu, and Zn, while the least affected were P, Mg, and Fe. We also found consistent differences among the coating technologies. Osmocote fertilizers released faster than specified at both high and low temperatures. Nutricote had relatively steady release rates over time and a nonlinear response to temperature. Polyon released more slowly than specified but replicate samples were highly uniform.

Key words: controlled release / Nutricote / Osmocote / Polyon / slow release

Accepted November 21, 2012

1 Introduction

1.1 Background

Plants obtain nutrients from the soil solution. Both the ratios and concentrations of nutrients in this solution influence uptake rates and efficiencies, impacting plant health. Addition of readily soluble, inorganic fertilizers to soil typically leads to solution nutrient concentrations higher than optimal for the plant and results in a potential for leaching losses and precipitation. Slow-release and controlled-release fertilizers (SRF and CRF, respectively) have been designed to improve the concentration of ions in the soil solution over specified growing periods. A comprehensive book on growing media (Handreck and Black, 2002) indicated that the terms “SRF” and “CRF” have been used interchangeably, but there is growing consensus that “CRF” should apply to polymer-coated fertilizers (PCF) while “SRF” applies to all other managed-release fertilizer products. Polymer-coated fertilizers (PCF) are the most advanced managed-release fertilizer technologies. Given their relatively high costs, PCF have largely been used for containerized plants and high-value field crops in high-leaching environments. One specialized application of PCF is the zero-leaching root zone of plants grown in space (Monje et al., 2003; Salisbury and Bugbee, 1985) and the challenges of long-term plant growth in this closed environment motivated this research.

To make PCF, fertilizer salts are aggregated into units called prills and polymer membranes are applied. Unique polymer-coating materials and manufacturing processes have been developed by several companies for each PCF type. Almost 20 years ago, Goertz (1993) described the composition and manufacturing processes of the coatings. Osmocote Plus, Nutricote Total with Minor Nutrients, and Polyon Coated NPK Plus are all categorized as polymer-coated fertilizers (Goertz, 1993). According to Goertz (1993), polymer coatings can be categorized as either thermoset resins or thermoplastic resins. Osmocote is listed as a thermoset resin, Nutricote is listed as thermoplastic resin, and the category of Polyon is not clear. The fertilizer companies use the terms “resin” and “polymer” interchangeably. In order to thoroughly understand the release of nutrients from PCF it is necessary to understand the theory and link it to the measurements published in the literature.

1.2 Mechanisms of nutrient release

In a recent assessment of polymer-coated materials (pharmaceuticals, in this case), Kaunisto et al. (2011) described multiple mechanisms of release, including diffusion, osmotic pumping (apparently caused by changes in hydrostatic pres-



* Correspondence: C. Adams; e-mail: curtis.b.adams@gmail.com

sure and an osmotic gradient), and convective release by coating disruption. According to Kaunisto et al. (2011), release occurs mainly by diffusion when the water potential is at steady-state and the coating material is permeable to the solutes within. Release by diffusion yields a relatively steady release, subject mainly to changes in coating permeability and temperature. The authors indicated that osmotic pumping (mass flow) and diffusion of solutes is likely when the coating is semipermeable to at least some solutes and cracks of limited volume are formed in the coating by the buildup of hydrostatic pressure. If the coating is completely impermeable to the internal solutes, there is no solute release until cracks are formed. Impermeability to fertilizer salts may be associated with swelling of the prill, although swelling may not be easily detectable. Finally, convective solute transfer by coating disruption would occur when the buildup of hydrostatic pressure causes coating rupture. This is the release mechanism for sulfur-coated urea, for example, and, as indicated by Shaviv et al. (2003a), likely happens in most PCF only due to coating failure.

Kaunisto et al. (2011) emphasized that targeted experimentation must be done in order to correctly identify mechanisms of release and also that the mechanism may change with the phases of the release process. The dominant release mechanism depends on the physical properties of the polymer coating and internal solutes, and their interactions with environmental conditions. Goertz (1993) reviewed PCF technologies and suggested that most PCF release nutrients purely by diffusion, mainly citing information from PCF manufacturers. Shaviv et al. (2003a) indicated that, due mainly to simplicity, most efforts to model PCF nutrient release have been based on some kind of diffusional control.

Shaviv et al. (2003a) proposed a conceptual model of nutrient release for individual PCF prills involving a three-phase process. The first of their proposed phases is a lag phase in which there is little to no nutrient release; during this phase water vapor diffuses into the prill and hydrates fertilizer salts. The authors indicated that the duration of the lag phase may depend on the time to hydrate internal voids in the prill or on the establishment of a steady state between influx of water and efflux of solutes. Hydrostatic pressure is generated within the coating in response to water uptake/mass increase. The second phase is a period of linear release in which the driving gradient for nutrient release by diffusion remains constant; this is due to the presence of undissolved fertilizer salts that maintain nutrient-saturated conditions in the solution within the prill relative to dilute ion concentrations in solution surrounding the prill. The authors indicated that nutrient movement across the coating may also occur by mass flow due to a pressure gradient, but did not discuss the conditions under which this would occur. Finally, there is a decay phase in which the nutrient-release rate declines due to a diminishing driving gradient as the concentration of fertilizer in solution decreases within the prill.

Kochba et al. (1990) suggested that the water-vapor pressure of the environment surrounding fertilizer prills determines release rates. While the initial water uptake would likely be faster in substrates with a higher water vapor pressure, a

hydrated prill would contain liquid water in previously air-filled spaces, blocking the movement of water vapor.

1.3 Empirical studies on nutrient release

Empirical data on nutrient release from populations of PCF prills (Broschat, 2005; Broschat and Moore, 2007; Du et al., 2006; Huett and Gogel, 2000) have shown significant deviation from the three-phase process proposed by Shaviv et al. (2003a) for single prills. In part, deviations have likely been observed because Shaviv et al. described release by diffusion only, whereas coating rupture, cracking, and mass flow are likely occurring to some extent in most PCF in empirical studies. Also, physical characteristics, such as fertilizer granule radius and coating thickness, are included in most models of nutrient release and are known to vary within populations of prills (Al-Zahrani, 1999; Du et al., 2004, 2008). Shaviv et al. (2003b) published a statistical model based on their single-prill work to enable scaling to physically heterogeneous populations of prills. The “size guide number” (SGN) and “uniformity index” (UI) are used in the fertilizer industry to quantify variance in prill size. In some cases, physical heterogeneity among populations of prills may be intentionally introduced by fertilizer manufacturers in order to achieve a desired release pattern. In an empirical study of individual Multicote® prills, Kochba et al. (1994) found extreme variability in release pattern among prills. The authors found differences in the time to onset of release as well as in release rates among prills. The authors proposed that populations of Multicote prills with heterogeneous release patterns may be the mechanism by which a desired prill-population release pattern is achieved in this fertilizer.

Broschat (2005), Broschat and Moore (2007), Du et al. (2006), and Huett and Gogel (2000) have identified the tendency of many PCF to release the bulk of their nutrients early, with generally decreasing release rates over time. These investigators also have shown the relative release rates of the primary macronutrients to generally be: $N > K > P$. Little has been reported on fundamental release characteristics of the other essential macro- and micronutrients. Broschat and Moore (2007) reported the release of Mg, Mn, and Fe to be poor, with less than 50% release of these elements in some cases. Albano et al. (2006) reported leaching rates of Ca, Mg, Fe, Mn, Zn, Cu, and Mo from chemically complex media containing different PCF types (Osmocote, Polyon, Multicote, and Nutricote). However, the media used by Albano et al. (2006) had significant chemical sorption/desorption potential for ions, which limits the usefulness of the data beyond applications in their specific media.

1.4 Environmental effects on nutrient release

Ideally, PCF would have nutrient-release rates that match plant nutrient demands, even when environmental conditions fluctuate. No current PCF meets this ideal, especially as nutrient release from PCF is affected by temperature. However, PCF are an improvement over other controlled-release options in that they are largely insensitive to biological activity, pH, and

substrate type or texture (Broschat, 2005; Kochba et al., 1990; Oertli and Lunt, 1962b; Shibata et al., 1980).

The reported effect of substrate water content on nutrient release has been inconsistent across studies. Kochba et al. (1990) reported that SRF (coated KNO_3 , produced by Haifa Chemicals Ltd., makers of Multicote) release was essentially equal at substrate moisture contents greater than 50% of field capacity in a sandy-loam soil. The investigators reported that their soil was near neutral in pH (7.3) and described a careful chemical extraction method for recovery of fertilizer ions from the soil; the test was conducted in sealed vials to ensure soil water-content stability over time. Others have reported PCF nutrient release to be faster in pure water than in moist, solid substrates, which is in contrast to the findings of Kochba et al. (1990). Shibata et al. (1980) reported Nutricote release to be 1.2 to 1.5 times faster when placed in pure water than when incorporated into a moist, solid substrate. These investigators tested release in a “sandy soil” but did not mention how they accounted for the potentially confounding chemical interactions of this substrate. Broschat (2005) reported that Osmocote and Nutricote release rates were slowest when surface-applied, intermediate when fully mixed into a moist substrate, and slightly faster when placed in pure water. Broschat’s experimental method may have affected the accuracy of his results, however. Fertilizer prills were placed into packets (for simple recovery) and inserted into complex media, potentially leading to limited water contact or altered water relations between the prills and the substrate solution. Du et al. (2006) concluded that nutrient release by Multicote into free water was somewhat faster than release into saturated sand and significantly faster than into sand at field capacity. But there is no theoretical basis for these differences, particularly for release in free water and saturated sand. The authors did not address potential chemical effects of their silica-sand substrate on their measurements.

Temperature affects PCF nutrient-release rates more than any other extrinsic factor. The dependence of nutrient release on temperature in CRF has been known since Oertli and Lunt (1962a) tested nutrient release from an unspecified CRF over a range of temperatures and reported a doubling in release for a 10°C rise in temperature (10% per °C). However, there is no consensus on the effect of temperature on PCF collectively or on individual PCF technologies in the recent literature. Husby et al. (2003) claimed that the effect of a diurnal temperature fluctuation on nutrient-release rate was a sensational 63.9% to 206.2% per °C (1278% to 4124% in total), depending on the PCF (Osmocote, Nutricote, and Polyon) when temperature was varied between 20°C and 40°C. Husby et al. (2003) reported that Osmocote was the most sensitive to temperature of the three technologies. Cabrera (1997) reported significant increases in N leaching as media temperature increased in pots of media containing Prokote®, a Polyon, and two Osmocote fertilizers (High Nitrogen and Fast Start). The author found lower rates of leaching with another Osmocote fertilizer, a Nutricote fertilizer, and a Woodace® fertilizer. In a study on Multicote, Kochba et al. (1994) observed an average increase in nutrient release over time of 5.5% per °C as temperature was raised from 30°C to 40°C. Also studying Multicote, Du et al. (2006) described a

decrease in the duration of the lag phase and an increase in release rate during the linear phase as a result of increasing temperature. In the linear release phase, calculations on the data of Du et al. (2006) show an average increase in release in water of 16% per °C as temperature increased from 20°C to 40°C, and an average of 18% per °C increase in the range of 20°C to 30°C. Huett and Gogel (2000) measured nutrient release of N, P, and K at 30°C and 40°C until 90% recovery in a study of 17 PCF—representing fertilizers from Nutricote, Apex Gold® (Polyon), Osmocote, and Macroco®. Nutrient-release dynamics with time were measured in their study, and the effect of temperature was quantified and reported as the time to reach 90% nutrient recovery, giving an average effect. Calculations on their data show an average increase in nutrient-release rates for all 17 fertilizers around 2% per °C (20% in total) when temperature was increased from 30°C to 40°C. Looking at the effect of temperature on individual nutrients in their study shows an average increase in N release to be $(2.6 \pm 1.2)\%$ per °C, $(1.5 \pm 0.9)\%$ per °C for P, and $(1.8 \pm 0.7)\%$ per °C for K. These data indicate that N may be more affected by temperature than either P or K and that variation in the temperature response among fertilizers may be significant (up to 60%). When the fertilizers were separated by type (brand) and analyzed, similar degrees of variation were found. The large variety in initial nutrient concentrations in the PCF that were tested may be part of the cause of this variation.

1.5 Objectives

Our summary of the literature led us to develop a conceptual model of nutrient release from PCF release based on physical principles, which builds on the conceptual model of Shaviv et al. (2003a). This conceptual model led us to hypothesize that there would be no difference in the release rates of PCF in water and a moist, solid substrate. A central objective was to test this hypothesis. Inconsistency in the literature makes it difficult to identify unique and common release characteristics among key PCF technologies. By studying fertilizers with similar initial concentrations of nutrients, another objective was to isolate the effect of three coating technologies on release rates of macro- and micronutrients, particularly as affected by temperature.

2 Material and methods

Three PCF types or technologies were investigated: Osmocote Plus (Grace Sierra Horticultural Products Co, Marysville, Ohio, USA), Nutricote Total with Minor Nutrients (Chisso-Asahi Fertilizer Company, LTD., Tokyo, Japan), and Polyon Coated NPK Plus (Pursell Industries, Sylacauga, Alabama, USA). These are widely used PCF types that represent some of the primary controlled-release polymer-coating technologies available and will hereafter be referred to simply as Osmocote, Nutricote, and Polyon. Seven fertilizers, representing shorter- and longer-term PCF, were studied. Initial fertilizer nutrient concentrations were matched as closely as possible (Tab. 1).

Table 1: The fertilizers investigated in these studies, representing three PCF types and a range of specified release timeframes. Fertilizers with similar balance of nutrients were selected to facilitate comparison of the nutrient-release characteristics of the three coating technologies. All nutrient concentrations are given in elemental form. Every Nutricote fertilizer has a uniform coating thickness, while Osmocote and Polyon fertilizers increase in coating thickness with increasing release duration. To achieve identical elemental analyses with differing coating thickness, it is our impression that fertilizer companies alter pill size.

PCF	Label	Timeframe		NO ₃ -N	NH ₄ -N	P	K	Mg	S	Fe	Mn	Zn	Cu	B
	N-P-K	/ months	(term)	/ % of total mass										
Osmocote	15-9-12	3 to 4	short	8	7	3.9	10	1.0	2.3	0.45	0.06	0.05	0.05	0.02
Osmocote	15-9-12	12 to 14	long	8	7	3.9	10	1.0	2.3	0.45	0.06	0.05	0.05	0.02
Nutricote	18-6-8	3 (T-100)	short	9.4	8.6	2.6	6.6	1.2	1.3	0.2	0.06	0.015	0.05	0.02
Nutricote	18-6-8	9 (T-270)	mid	9.4	8.6	2.6	6.6	1.2	1.3	0.2	0.06	0.015	0.05	0.02
Nutricote	18-6-8	12 (T-360)	long	9.4	8.6	2.6	6.6	1.2	1.3	0.2	0.06	0.015	0.05	0.02
Polyon	16-6-13	1 to 2	short	7.2	8.8	2.6	10.8	1.4	6.7	0.33	0.13	0.080	0.080	0
Polyon	15-6-11	10 to 12	long	6.7	8.3	2.6	9.1	1.3	6.1	0.31	0.12	0.074	0.074	0

2.1 Nutrient release from PCF in water

Thirteen replicate samples of 6.5 g of the “long-term”-rated PCF listed in Tab. 1 (with the exception of Nutricote, where “mid-term” was used) were placed in 250 mL flasks with 200 mL of deionized water (32.5 g L⁻¹). Electrical conductivity of the water was measured once each week immediately following gentle swirling of the flask (Hanna Instruments, model HI 8733 conductivity meter with temperature compensation). After measurement, the water was decanted and replaced with deionized water. Replicate water samples were periodically pooled and analyzed for nutrients using ICP-OES speciation analysis (Thermo IRIS Intrepid II, Thermo Scientific Inc., Waltham, MA). The flasks were placed at room temperature ([23 ± 1.4]°C), and measurements were taken over the course of about 400 d. Short-term (30 d) measurements of release rates by electrical conductivity were also taken on single prills by placing ten randomly selected prills into individual tubes containing 30 mL of deionized water; the water was not renewed over the 30 d timeframe.

The effects of chemical complexation and ion pairing are known to affect electrical-conductivity measurements. The response of electrical conductivity to increasing ion concentration is not linear due to these effects, leading to underestimates when ion concentrations are high. But measuring electrical conductivity, which integrates the effects of all ionic species in solution, is useful to simplify comparison of broad trends in nutrient release among fertilizers. We chose fertilizers with similar elemental ratios to make these comparisons as valid as possible.

The test conducted on populations of fertilizer prills (32.5 g L⁻¹) was repeated at a range of temperatures (5°C, 15°C, 20°C, 30°C, and 40°C), including all fertilizers listed in Tab. 1. There were three replicate samples of each fertilizer for each temperature treatment (105 samples). This study was conducted in temperature-controlled boxes with circulating fans. Temperature was monitored and controlled to within ± 0.2°C by thermocouples connected to a Campbell Scientific

CR1000 datalogger. Before electrical-conductivity measurement, the fertilizer solutions were allowed to come within 5°C of room temperature in order to minimize measurement error. The fertilizer prills were left in solution during temperature equilibration, but this period did not exceed 30 min (less than 0.3% of the weekly release time). Temperature equilibration was necessary because, despite temperature compensation in the electrical-conductivity meter, measurements were found to slowly drift when solution temperature significantly differed from ambient temperature. Replicate water samples from the 15°C, 20°C, 30°C, and 40°C treatments were periodically pooled and analyzed for nutrients using ICP-OES speciation analysis and colorimetric nitrate and ammonium tests (LaMotte Smart Colorimeter, Chestertown MD). After 105 d of incubation in water, the fertilizers were dried at 105°C for 7 d to quantify the mass of nutrients that had been expended from the fertilizers at each temperature. A temperature of 105°C was used to remove water without causing chemical transformations (James and Wells, 1990). Estimation of the mass of the polymer coatings was necessary. In order to quantify the coatings, 30 g of each fertilizer were ground in a blender with 2 L of water, dissolving as much nutrient salt as possible. A beaker and a piece of solid nylon mesh were preweighed. The fertilizer mixture was poured through the mesh, capturing the coating while allowing all water and soluble material to flow through. Any fertilizer that was not in solution was left in the blender, additional water was added, and the procedure was repeated until all fertilizer was in solution and all coating material was recovered in the mesh. The mesh was placed in its preweighed beaker, dried for 2 d at 80°C and weighed again.

2.2 Nutrient release from PCF in chemically inert sand

The chemical sorption/desorption properties of a substrate alter bio-available nutrient concentrations after release from PCF, so a chemically inert substrate is necessary to rigorously determine ion-release rates. Therefore, our studies

were carried out in columns of pure silica sand (medium-grained Ottawa sand). This sand, obtained from quarries near Ottawa, IL (USA) is recognized for its chemical inertness and is often used as a lower-cost alternative to glass beads. Measurements in our lab have shown it to have minimal adsorption of anions and cations and minimal pH-buffering capacity (Henry et al., 2006). More than 95% of the sand particles had diameters from 0.5 to 0.6 mm.

PVC columns (3.8 cm or 1.5 cm in diameter) were cut to contain 500 cm³ of the Ottawa sand with fertilizer. The long-term-rated PCF listed in Tab. 1 were used (with the exception of Nutricote, where mid-term was used). Fertilizer samples (6.5 g per column) were uniformly mixed into individually measured allotments of sand and placed into the columns (filled to a height of \approx 44 cm). There were three replicate columns per fertilizer treatment. The bottom of each column was fitted with a PVC slip coupler, which held a section of landscape fabric that contained the substrate while allowing free percolation of water and solutes. To prevent evaporation, a PVC slip cap was put on the top of each column, and a water-impermeable plug of closed-cell foam was inserted into the coupler at the bottom.

To start the PCF nutrient-release process and to flush any residual salts off the sand, 500 mL of deionized water were added to each column and the leachate was discarded. To provide the same ratio of fertilizer to water as in the water-release test (described earlier), each week 200 mL water were added to the top of each column and the leachate was collected. With each measurement, the columns were

allowed to drain completely (\approx 20 min) to prevent water from standing at the bottom of the columns. Leachate recovery was 97% or higher (\geq 194 mL out of 200 mL). The electrical conductivity of the leachate was measured each week. The study was conducted at room temperature ($[23 \pm 1.4]^\circ\text{C}$) over the course of about 400 d.

Water-retention measurements on the sand showed that after complete drainage, volumetric water contents ranged from 0.33 cm³ cm⁻³ at the bottom to 0.04 cm³ cm⁻³ at the top (0 to 44 cm, respectively). The average volumetric water content was 0.13 cm³ cm⁻³, with a total water volume of \approx 65 mL. The water potential ranged from \approx 0 at the bottom to -4.4 kPa at the top. Similar to plants grown in well-watered containers or soil, none of the prills that were added to the columns were exposed to low water potentials.

3 Results

3.1 Conceptual model of nutrient release

When water diffuses into PCF prills and hydrates fertilizer salts, air-filled spaces in the coating are filled with solution, providing liquid paths for outward diffusion of nutrient ions. Except in extremely dry soils (< -1.5 MPa water potential) humidity remains near saturation (Robarge, 1999); a constant water-potential environment above approximately -1.5 MPa would maintain hydration of the prills. In the absence of environmental changes, once the prill is hydrated, there would be no flux of water across the coating; nutrient ions, not nutrient solution, would exit PCF prills. Steady-state nutrient release

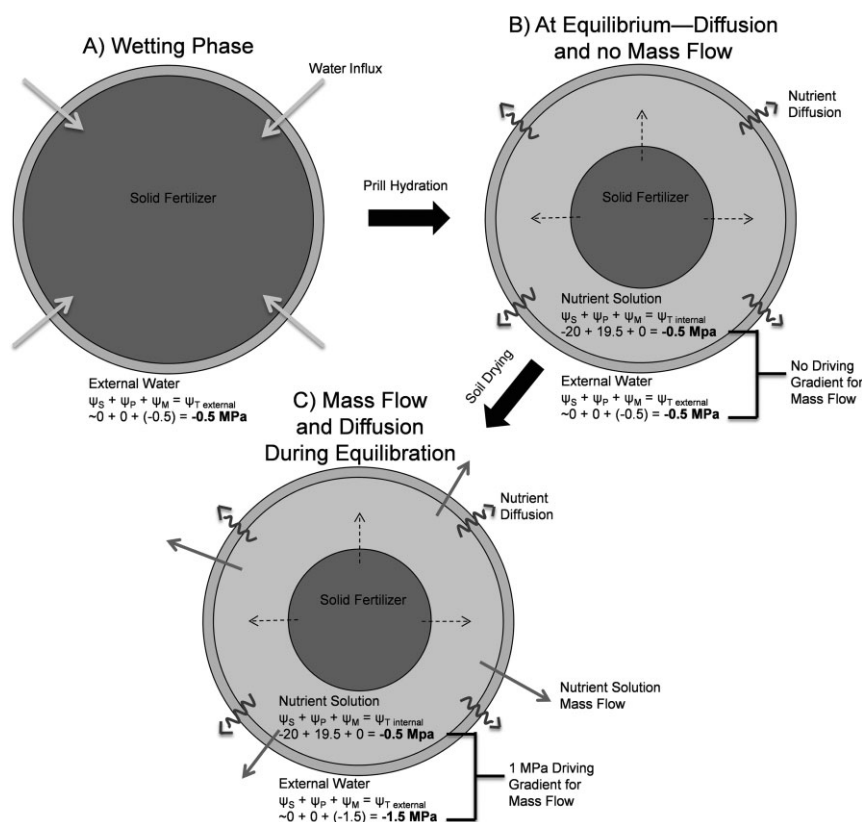


Figure 1: Water-potential dynamics between a fertilizer prill and its environment. Ψ_s is the solute potential, Ψ_p is the pressure potential (hydrostatic pressure), Ψ_M is the matric potential, and Ψ_T is the total water potential (Nobel, 2009). Water influx is driven by a gradient in total water potential. As the prill becomes hydrated the air-filled spaces in the coating become filled with solution, providing a liquid path for outward diffusion of nutrient ions. Equilibrium values are shown. As the total water potential of the environment decreases from -0.5 MPa to -1.5 MPa, some hydrostatic pressure is relieved within the prill causing outward mass flow of nutrient solution. The opposite would happen in response to environmental wetting.

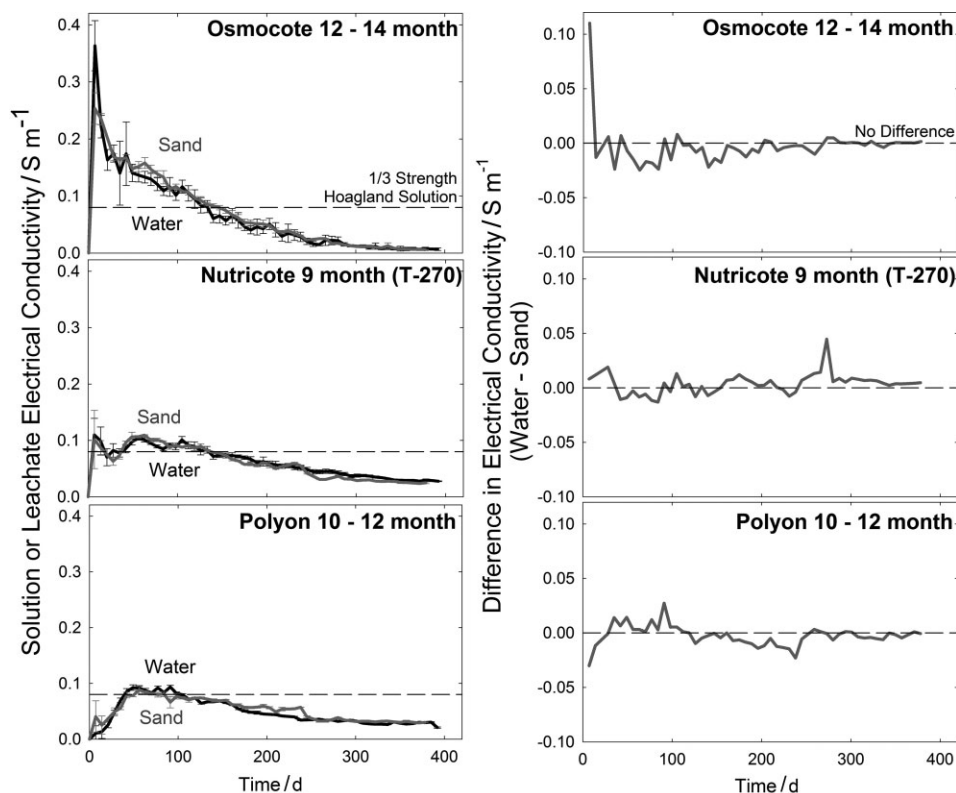


Figure 2: Left: Nutrient-release profiles for three PCF as measured by electrical conductivity in flasks of water and in the leachate of columns of chemically inert Ottawa sand. Each measurement represents a week of nutrient release from 6.5 g of fertilizer collected in 200 mL of deionized water (32.5 g L⁻¹). A line indicating 1/3-strength Hoagland solution, widely considered an optimal nutrient solution, has been inserted as a reference. Error bars represent standard deviation. Right: The difference in electrical conductivity measured between fertilizer release in water and columns of sand, which shows no consistent or significant difference for any PCF.

by diffusion is driven by ion-concentration gradients across the polymer coating. The water-potential dynamics between a representative prill and its environment are shown in Fig. 1. Figure 1A shows initial hydration of a fertilizer prill in a moist

soil condition, and Fig. 1B shows outward diffusion of nutrients at an equilibrium state. In addition to ion-concentration gradients, the rate of nutrient diffusion would depend on temperature and on the permeability of the polymer-coating tech-

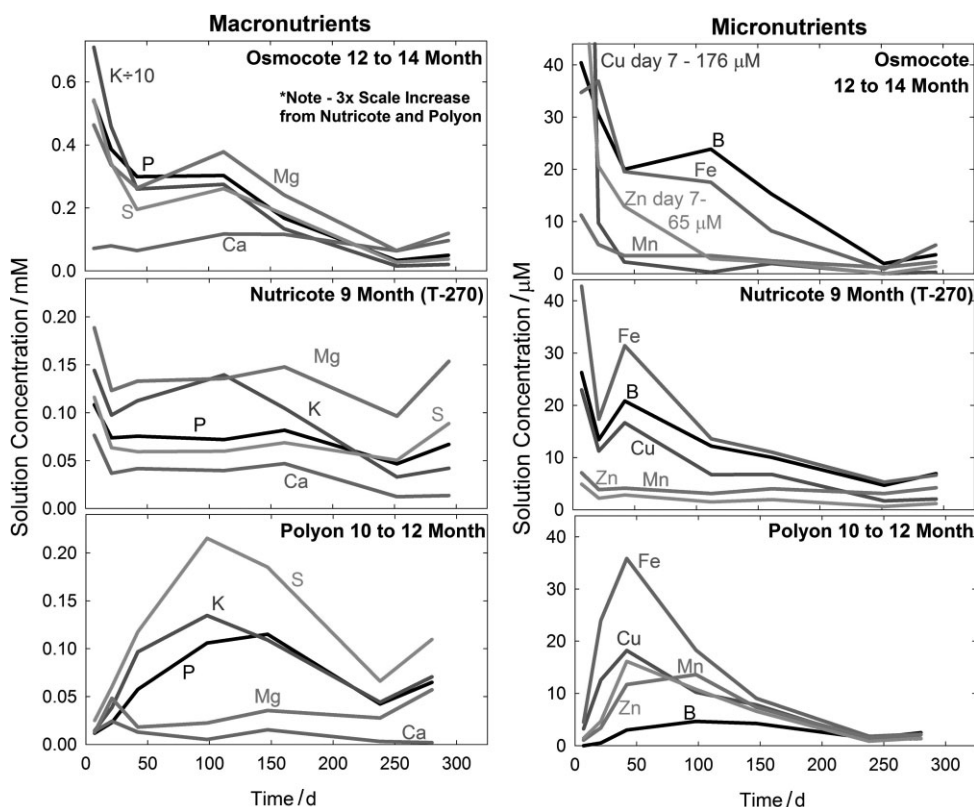


Figure 3: Nutrient concentrations over time in flasks of water containing three PCF at a rate of 32.5 g PCF L⁻¹. Each point represents fertilizer release for 1 week. For Osmocote, K values were divided by 10, and Cu and Zn were allowed to go off scale due to large values. The release of these ions from Osmocote was exceptionally rapid and required rescaling of the top left graph.

nology. The permeability of individual polymer types may be differentially affected by temperature and other environmental factors.

Mass flow of water would be expected to occur in response to changes in the water-potential gradient across the coating—mass flow of water inward in response to wetting and mass flow outward during drying. This mass flow would occur even in the absence of cracks in the coating. Figure 1C shows mass flow of solution from the prill in response to drying. In a non-steady-state, fluctuating-water-potential environment, the mass flow of solution across the coating could lead to higher overall rates of nutrient release relative to a constant environment (such as release in pure water). PCF with more elastic coating materials that expand in size might be expected to have larger-volume mass-flow events and faster nutrient release in a fluctuating-water-potential environment.

3.2 Effect of substrate water content

For longer-term-rated PCF, nutrient-release rates in moist, chemically inert sand and pure water were not significantly different, as shown by electrical-conductivity measurements at weekly intervals (Fig. 2). This result is consistent with the conceptual model shown in Fig. 1 which indicates that, despite differences in water potential, nutrient-release rates will be the same if the water potentials are constant and sufficiently high. Measurements of the release of individual nutrients (excluding nitrogen) in water are shown for nearly 300 d in Fig. 3.

3.3 Nutrient-release trends and the effect of temperature

Nutrient-release trends over a range of temperatures are summarized by measurements of electrical conductivity in Fig. 4. The effects of chemical complexation and ion pairing

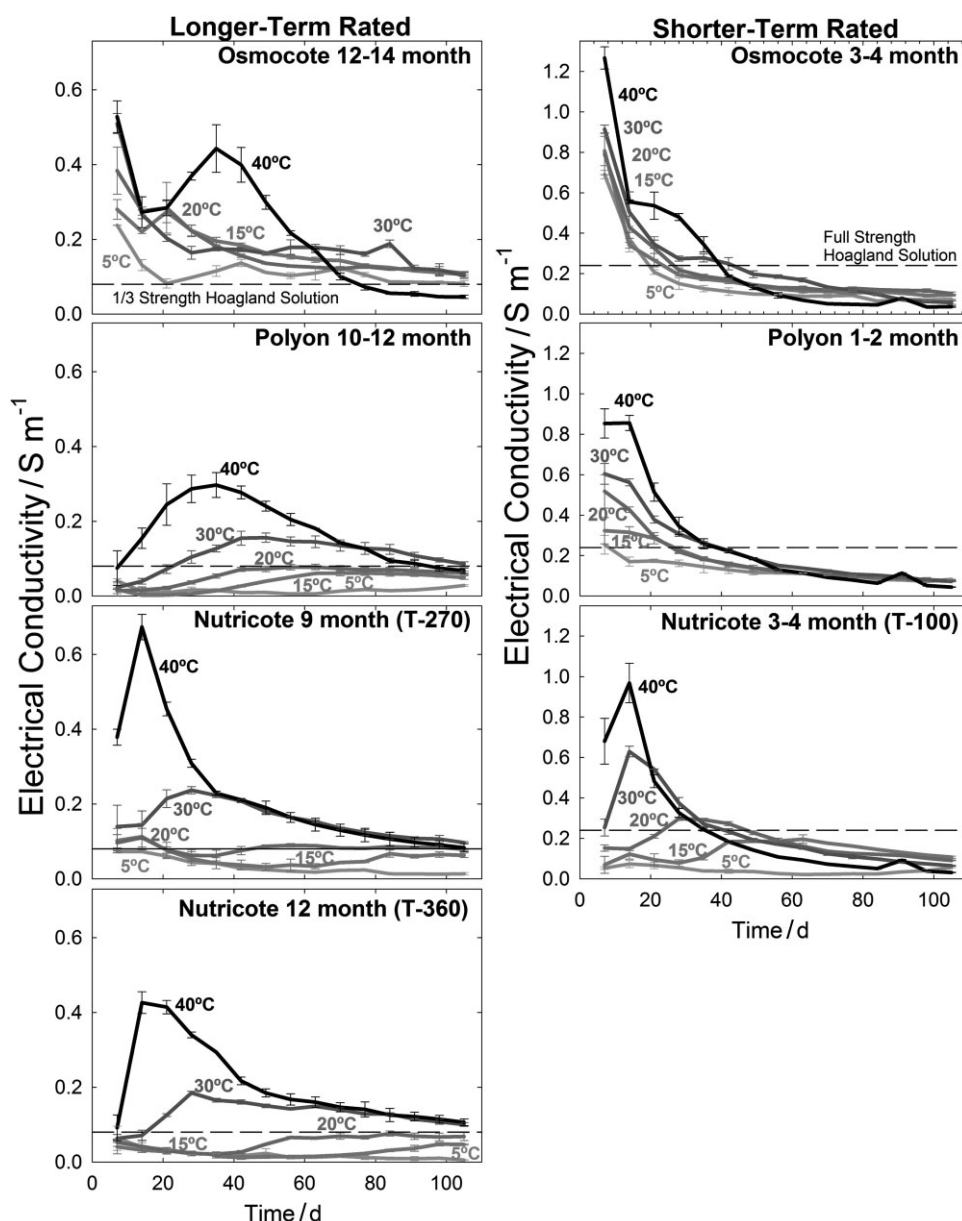


Figure 4: Nutrient-release profiles for seven PCF as measured by electrical conductivity in flasks of water. Each measurement represents a week of nutrient release from 6.5 g of fertilizer in 200 mL of deionized water (32.5 g L⁻¹) at five temperatures. A line for 1/3-strength Hoagland solution, widely considered an optimal nutrient solution, has been inserted as a reference for the longer-term-rated fertilizers. A line for full-strength Hoagland solution has been inserted as a reference for the shorter-term fertilizers. Error bars represent standard deviation.

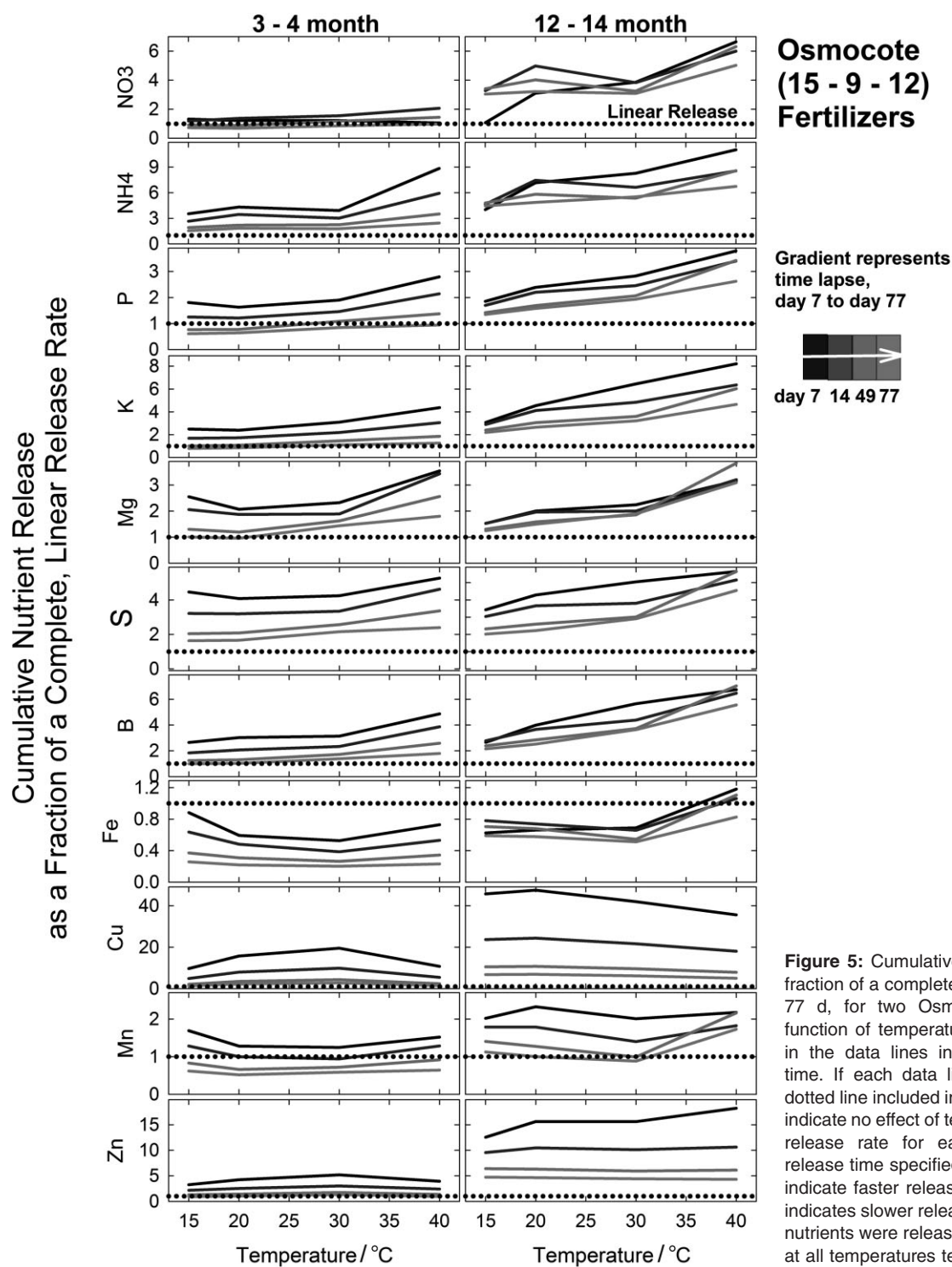


Figure 5: Cumulative nutrient release as a fraction of a complete, linear release rate for 77 d, for two Osmocote fertilizers as a function of temperature. The color gradient in the data lines indicates progression in time. If each data line fell directly on the dotted line included in the graphs, this would indicate no effect of temperature and a linear release rate for each nutrient over the release time specified; above the line would indicate faster release, while below the line indicates slower release. In Osmocote, most nutrients were released faster than specified at all temperatures tested.

are known to affect electrical-conductivity measurements. The response of electrical conductivity to increasing ion concentration is not linear due to these effects, leading to underestimates when ion concentrations are high. But measuring electrical conductivity, which integrates the effects of all ionic species in solution, is useful to simplify comparison of broad trends in nutrient release among fertilizers. We chose fertilizers with similar elemental ratios to make these comparisons as valid as possible.

Individual ion concentrations, measured at 14 d intervals, are summarized in Figs. 5, 6, and 7 as a function of temperature. These data are summarized as cumulative nutrient release relative to a complete, linear release of each nutrient over the release timetable specified for each fertilizer. Ion measurements were summarized cumulatively because, ideally, leaching from any growth system would be minimized. A snapshot of the effect of temperature after 105 d of release is shown in Fig. 8. The most relevant summaries are included

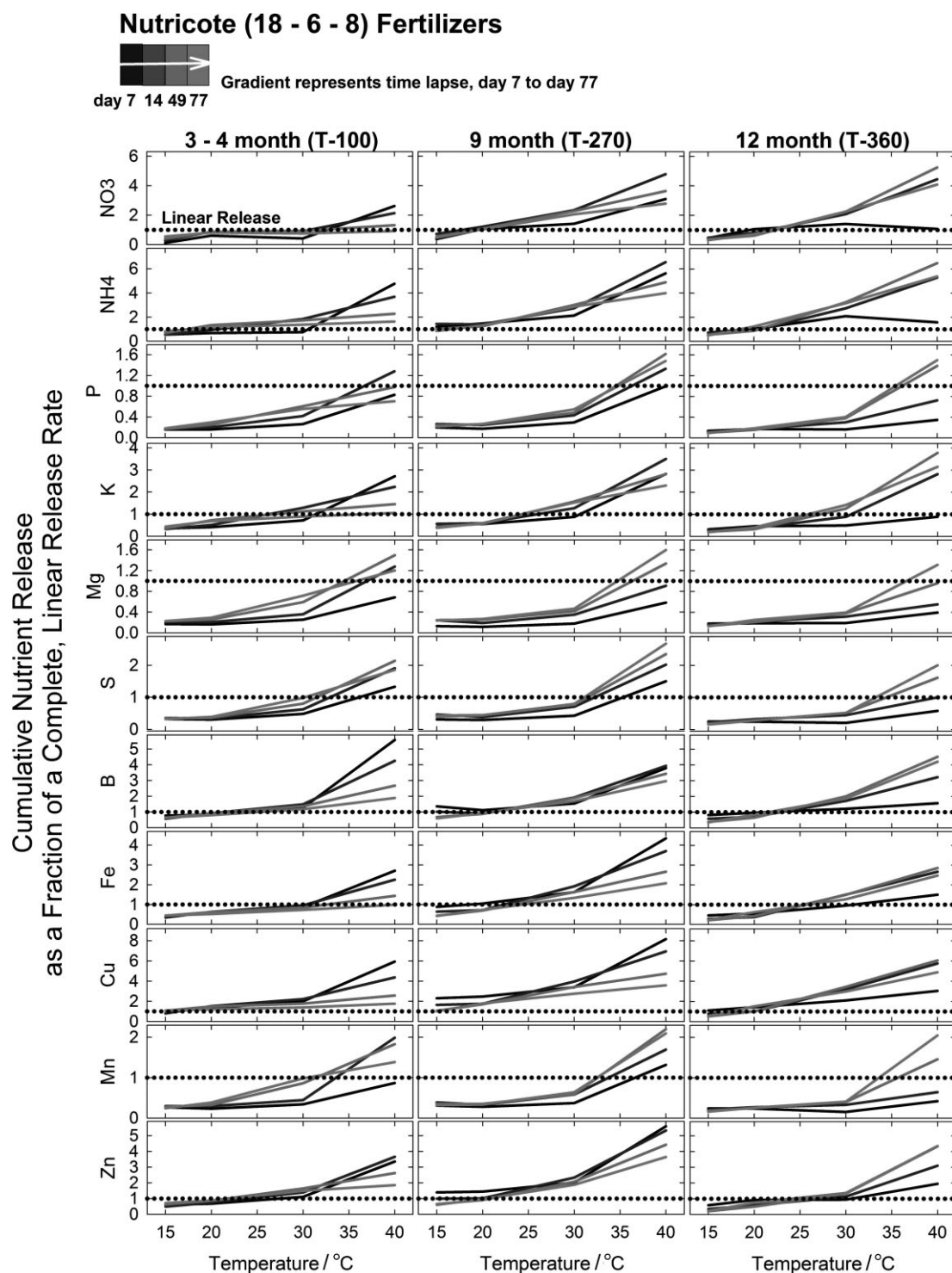


Figure 6: Cumulative nutrient release as a fraction of a complete, linear release rate for 77 d, for three Nutricote fertilizers as a function of temperature. The color gradient in the data lines indicates progression in time. If each data line fell directly on the dotted line included in the graphs, this would indicate no effect of temperature and a linear release rate for each nutrient over the release time specified; above the line would indicate faster release, while below the line indicates slower release. In Nutricote, nutrient release was strongly and nonlinearly dependent on temperature.

here, but there are numerous ways to graphically summarize these data; additional time/temperature graphs are available in Adams (2010).

Longer-term-release fertilizers were more strongly affected by temperature than shorter-term fertilizers. Higher temperatures generally led to an earlier and higher peak in nutrient-release rates. Across all fertilizers, the nutrients most strongly affected by temperature were typically N, K, B, Cu, and Zn,

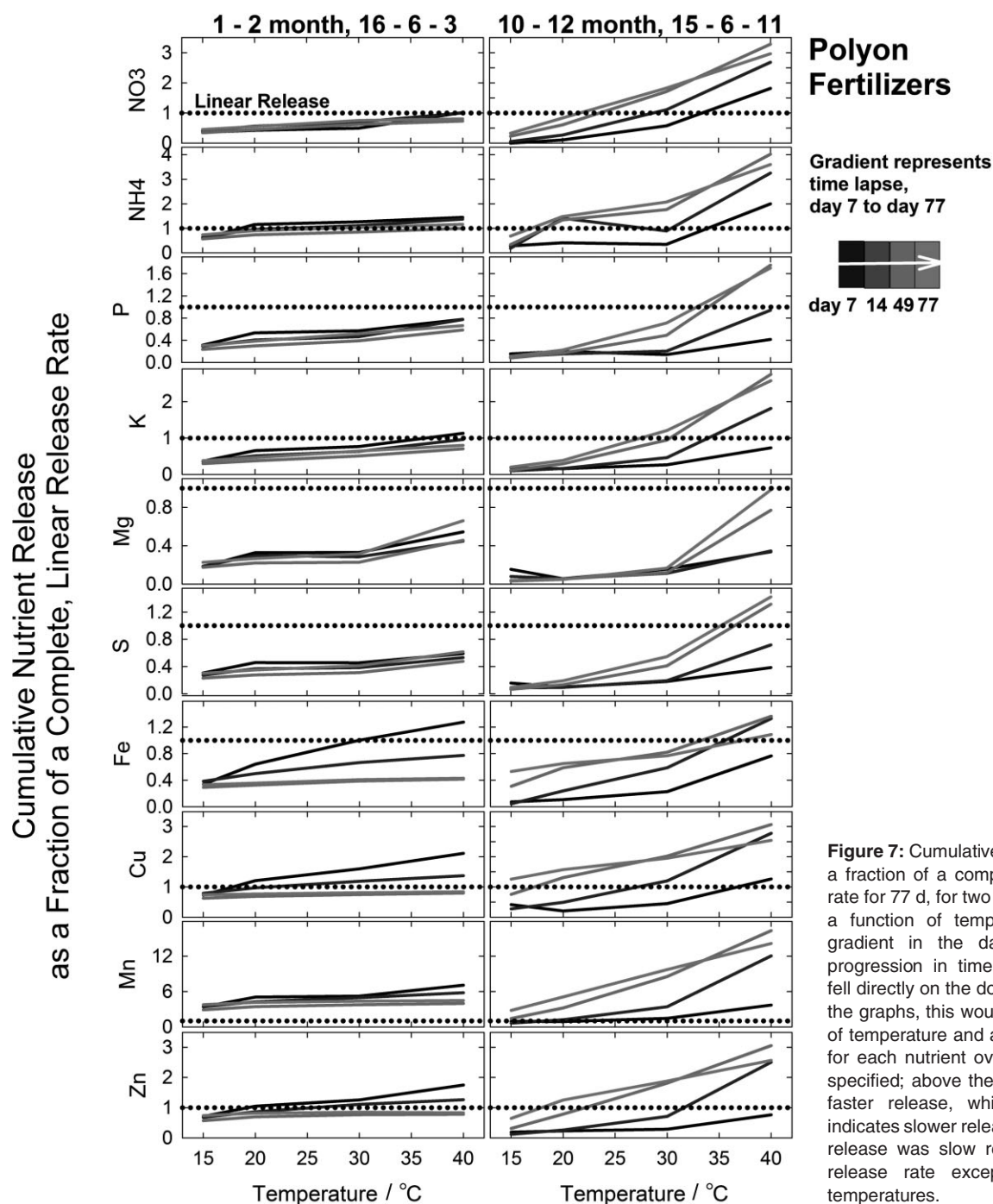


Figure 7: Cumulative nutrient release as a fraction of a complete, linear release rate for 77 d, for two Polyon fertilizers as a function of temperature. The color gradient in the data lines indicates progression in time. If each data line fell directly on the dotted line included in the graphs, this would indicate no effect of temperature and a linear release rate for each nutrient over the release time specified; above the line would indicate faster release, while below the line indicates slower release. Polyon fertilizer release was slow relative its specified release rate except at the highest temperatures.

while the least affected were P, Mg, and Fe. Because the effect of temperature on individual nutrients could be generalized across all PCF types, it is likely that the effects are caused by differences in elemental solubility and concentration.

There were also consistent differences among coating technologies in release rate. Osmocote tended to release nutrients more rapidly than specified at all temperatures. Contrary to other reports, our data indicate nutrient release in Osmocote had the least dependence on temperature, based on the

percentage change in release rate with temperature. The response to temperature was generally linear and averaged 3.6% per °C increase in release in the longer-term fertilizer and 1.3% per °C in the shorter-term fertilizer (for all nutrients, from 15°C to 40°C, for 105 d). Initial rapid nutrient release was followed by a steadily decreasing rate of release over time. Cu and Zn were purged exceptionally rapidly, with release of these nutrients nearly ceasing after the first week. Iron was the only nutrient that was not released at a faster rate than specified. Many Osmocote prills swelled up to twice their original size after hydration, and this was especially pre-

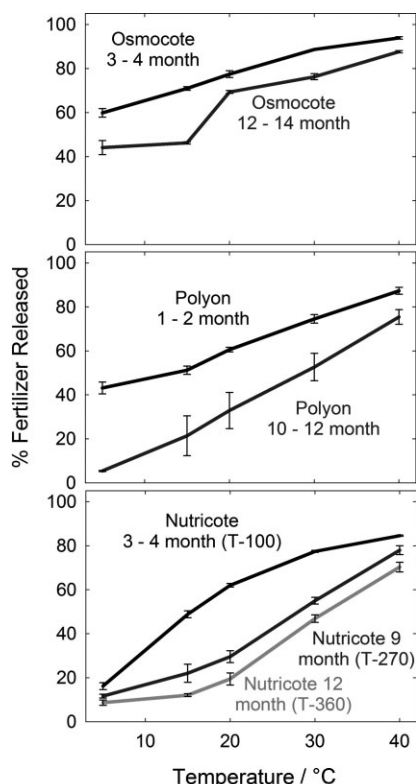


Figure 8: The percent of nutrient salts expended, based on change in mass, from Osmocote, Nutricote, and Polyon fertilizers incubated in water from 5°C to 40°C for 105 d (3.5 months). The values of percent polymer coating used in preparation of these graphs are as follows: Nutricote (all release rates)—11%; Polyon 1 to 2 month—7%; Polyon 10 to 12 month—14%; Osmocote 3 to 4 month—10%; and Osmocote 12 to 14 month—15%. Error bars represent standard deviation.

valent at higher temperatures. Osmocote Plus includes prills varying in shades of color from yellow to light green. Our tests on individual prills suggested that prills with greener color had more rapid release rates, while those that were more yellow were slower. Mixing prills with different release rates may be used to achieve a desired release profile over time.

In Nutricote, nutrient release was nonlinearly dependent on temperature. The effect of temperature on nutrient release was particularly strong between 20°C and 40°C where increases averaged 13.1% per °C for T-360, 8.2% per °C for T-270, and 1.8% per °C for T-100 (for all nutrients, for 105 d). The small effect of temperature in T-100 is partially due to the cessation of nutrient release before 105 d at higher temperatures. The effect of temperature on each Nutricote fertilizer was more uniform across all nutrients than in any other PCF type. There was minimal nutrient release in the fertilizers at lower temperatures (5°C to 15°C). Steady-state nutrient release was most effectively achieved in the mid-temperature range (20°C to 30°C). Similar to the observation in Osmocote, Nutricote fertilizers included prills that were distinctly faster or slower in release; unlike Osmocote, all Nutricote prills had a uniform appearance.

Nutrient release rates from Polyon were generally slower than specified, except at the highest temperatures. Lower

temperatures virtually stopped release in the longer-term fertilizer, while release was more significant in the shorter-term fertilizer at these temperatures. Peak release rates for most nutrients were delayed 20 to 40 d in the longer-term fertilizer. Measurements of the electrical conductivity of solutions containing single Polyon prills showed that every prill had a significant lag phase before any nutrients were released and a high degree of uniformity. The response to temperature was generally linear and averaged 10.1% increase in release per °C in the longer-term fertilizer and 2.8% per °C in the shorter-term fertilizer (for all nutrients, from 15°C to 40°C, for 105 d). Manganese was released especially rapidly.

3.4 Variability among replicate prill populations

The coefficient of variation (standard deviation divided by the mean) was calculated on the water data in Fig. 2 to determine the uniformity of release among replicate prill populations (Fig. 9). This test included 13 replicate samples per fertilizer type. Replicate samples of Polyon had the least variability of the three PCF types, generally below 5%. The variability in Nutricote was generally 10% or lower. The variability in Osmocote was erratic, with an increasing trend over time from about 10% to about 40%.

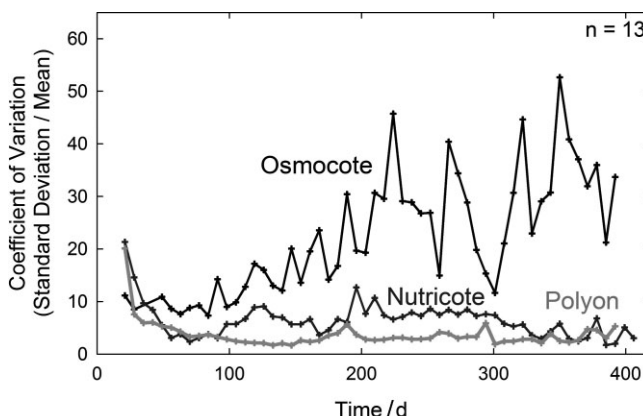


Figure 9: Variation among 13 replicate beakers for the three long-term-release fertilizers based on the water data in Fig. 3. Variability in Polyon was generally less than 5%, and was less than 10% in Nutricote. The trend in variability in Osmocote was erratic, generally increasing over time from about 10% to about 40%.

4 Discussion

The conceptual model presented here extends previous models and clearly describes the driving gradients for nutrient release, the effects of environmental parameters, and the conditions under which mass flow of solution across polymer coatings would be expected. Contrary to several empirical studies, our data are consistent with our water-potential model and indicate that there is no significant difference in nutrient-release rates of PCF in water and a moist, solid substrate. This finding indicates that our results can be used to model optimal fertilizer-application rates in substrates where chemical sorption/desorption properties may alter bio-available nutrient concentrations after release.

In Osmocote, our data indicate relatively rapid release rates at all temperatures; initial rapid nutrient release was followed by a steadily decreasing rate of release over time. In an applied sense, this release trend would lead to an early overload of root-zone nutrients and potentially cause deficiencies of nutrients later (in a system with leaching). The swelling observed in Osmocote prills likely leads to increases in nutrient-release rates due to pore expansion; expansion of the pores would increase mass flow across the coating. The erratic variability in the release rate of Osmocote may also be related to the swelling of prills, if swelling led to random prill rupture and abrupt changes in nutrient-release rates. The purging of Cu and Zn from Osmocote may lead to early toxicities or later deficiencies of these nutrients.

Nutricote fertilizers were the most effective at delivering steady-state release of nutrients in the mid-temperature range (20°C to 30°C). The strong effect of temperature, particularly between 30°C and 40°C, may lead to a large, early delivery of nutrients and nutrient deficiencies later (in a system with leaching). The virtual cessation of nutrient release at low temperatures suggests that all Nutricote fertilizers, including T-100, may overwinter well in cold environments as long as freezing does not result in cracking of the polymer coating. The observation of faster- and slower-release prills within a population suggests that a mix of prills with different release rates could be used to control release rate over time.

The release rate of Polyon fertilizers was generally slower than specified, except at the highest temperatures (30°C to 40°C). The significant lag phase of 20 to 40 d for most nutrients in the longer-term-rated fertilizer would likely lead to plant nutrient deficiencies. After reaching its peak release rate, the release profile of Polyon looked generally similar to that of Nutricote in the mid-temperature range (20°C to 30°C)—relatively flat over time. Like Nutricote, only slight release at lower temperatures in the longer-term fertilizer suggests that this fertilizer may overwinter well; release was more significant in the shorter-term fertilizer at lower temperatures. The high degree of uniformity among Polyon prills may lead to uniformity among replicate containers in which the fertilizer is used.

Acknowledgments

This research was funded by a grant from NASA and supported by the USDA-ARS. We thank Douglas Sturtz and Russell Friedrich for assistance with nutrient analysis. This research was also supported by the Utah Agricultural Experiment Station, Utah State University, and approved as journal paper number 8405.

References

- Adams, C. B. (2010): Optimizing the physical and nutritional environment of closed root-zones. Masters thesis, Utah State University, Logan UT, available online at: <http://usu.edu/cpl/PDF/CurtisAdamsMSThesis.pdf>
- Al-Zahrani, S. M. (1999): Controlled-release of fertilizers: Modeling and simulation. *Int. J. Eng. Sci.* 37, 1299–1307.
- Albano, J. P., Merhaut, D. J., Blythe, E. K., Newman, J. P. (2006): Nutrient release from controlled-release fertilizers in a neutral-pH substrate in an outdoor environment: II. Leachate calcium, magnesium, iron, manganese, zinc, copper, and molybdenum concentrations. *Hort. Sci.* 41, 1683–1689.
- Broschat, T. K. (2005): Rates of ammonium-nitrogen, nitrate-nitrogen, phosphorus, and potassium from two controlled-release fertilizers under different substrate environments. *Hort. Technol.* 15, 332–335.
- Broschat, T. K., Moore, K. K. (2007): Release rates of ammonium-nitrogen, nitrate-nitrogen, phosphorus, potassium, magnesium, iron, and manganese from seven controlled-release fertilizers. *Commun. Soil Sci. Plan.* 38, 843–850.
- Cabrera, R. I. (1997): Comparative evaluation of nitrogen release patterns from controlled-release fertilizers by nitrogen leaching analysis. *Hort. Sci.* 32, 669–673.
- Du, C., Zhou, J., Shaviv, A., Wang, H. (2004): Mathematical model for potassium release from polymer-coated fertilizers. *Biosyst. Eng.* 88, 395–400.
- Du, C., Zhou, J., Shaviv, A. (2006): Release characteristics of nutrients from polymer-coated compound controlled release fertilizers. *J. Polym. Environ.* 14, 223–230.
- Du, C., Tang, D., Zhou, J., Wang, H., Shaviv, A. (2008): Prediction of nitrate release from polymer-coated fertilizers using an artificial neural network model. *Biosyst. Eng.* 99, 478–486.
- Goertz, H. M. (1993): Controlled release technology (agricultural), in Kirk-Othmer: Encyclopedia of Chemical Technology. 4th edn., John Wiley & Sons, Inc., New York, pp. 266–274.
- Handreck, K., Black, N. (2002): Growing media. UNSW Press, Sydney Australia, p. 542.
- Henry, A., Doucette, W., Norton, J., Jones, S., Chard, J., Bugbee, B. (2006): An axenic plant culture system for optimal growth in long-term studies. *J. Environ. Qual.* 35, 590–598.
- Huett, D. O., Gogel, B. J. (2000): Longevity and nitrogen, phosphorus, and potassium release patterns of polymer-coated controlled-release fertilizers at 30°C and 40°C. *Commun. Soil Sci. Plan.* 31, 959–973.
- Husby, C. E., Niemiera, A. X., Harris, J. R., Wright, R. D. (2003): Influence of diurnal temperature on nutrient release patterns of three polymer-coated fertilizers. *Hort. Sci.* 38, 387–389.
- James, D. W., Wells, K. L. (1990): Soil sample collection and handling: technique based on source and degree of variability, in Soil Testing and Plant Analysis. Soil Science Society of America, Madison, WI, USA, pp. 25–43.
- Kaunisto, E., Marucci, M., Borgquist, P., Axelsson, A. (2011): Mechanistic modeling of drug release from polymer-coated and swelling and dissolving polymer matrix systems. *Int. J. Pharm.* 418, 54–77.
- Kochba, M., Gambash, S., Avnimelech, Y. (1990): Studies on slow release fertilizers: I. Effects of temperature, soil moisture, and water vapor pressure. *Soil Sci.* 149, 339–343.
- Kochba, M., Gambash, S., Avnimelech, Y. (1994): Slow release rate: individual granules and population behavior. *Fertil. Res.* 39, 39–42.
- Monje, O., Stutte, G. W., Goins, G. D., Porterfield, D. M., Bingham, G. E. (2003): Farming in space: Environmental and biophysical concerns. *Adv. Space Res.* 31, 151–167.
- Nobel, P. S. (2009): Physicochemical and environmental plant physiology. Academic Press, Boston, MA, p. 582.
- Oertli, J. J., Lunt, O. R. (1962a): Controlled release of fertilizer minerals by encapsulating membranes: I. Factors influencing the rate of release. *Soil Sci. Soc. Am. J.* 26, 579–583.

- Oertli, J. J., Lunt, O. R. (1962b): Controlled release of fertilizer minerals by encapsulating membranes: II. Efficiency of recovery, influence of soil moisture, mode of application, and other considerations related to use. *Soil Sci. Soc. Am. J.* 26, 584–587.
- Robarge, W. P. (1999): Precipitation/dissolution reactions in soils, in Sparks, D. L. (ed.): *Soil Physical Chemistry*. CRC Press, Boca Raton, pp. 193–233.
- Salisbury, F., Bugbee, B. (1985): Wheat farming in a lunar base, in: *Lunar Bases and Space Activities of the 21st Century*. Lunar and Planetary Institute, Houston TX, USA, pp. 635–645.
- Shaviv, A., Smadar, R., Zaidel, E. (2003a): Modeling controlled nutrient release from polymer coated fertilizers: Diffusion release from single granules. *Environ. Sci. Technol.* 37, 2251–2256.
- Shaviv, A., Smadar, R., Zaidel, E. (2003b): Modeling controlled nutrient release from a population of polymer coated fertilizers: Statistically based model for diffusion release. *Environ. Sci. Technol.* 37, 2257–2261.
- Shibata, A., Fujita, T., Maeda, S. (1980): Nutricote-coated fertilizers processed with polyolefin resins. *Acta Hort.* 99, 179–186.